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Primary Evaluator

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Registration Action Branch 1

(RAB1)

Health Effects Division

(HED) (7509C)

## **STUDY REPORT:**

MRID No. 455560-03 C.A. Green (2001) Magnitude of the Residues of Pyriproxyfen on Cabbage. Laboratory Project Identification Number: 20221. Unpublished study prepared by Valent USA Corporation. 180 pages.

## **EXECUTIVE SUMMARY:**

Supervised crop field trials were conducted in California (2 trials), Florida, North Carolina, Pennsylvania, Texas, and Wisconsin in/on cabbage treated two times at an application rate of 0.066 lb ai/A (seasonal rate of 0.132 lb a.i./A) with a pre-harvest interval (PHI) of 6-7 days and a retreatment interval (RTI) of 14 days. The results from these trials show that pyriproxyfen residues ranged from 0.04-0.49 and <0.01-0.02 ppm in/on treated cabbage samples with and without wrapper leaves, respectively. Pyriproxyfen residues demonstrated a slight decline with increasing PHI over a range of 3-14 days. Doubling the application rate appeared to have little affect on the pyriproxyfen residue level. However, the PHI and application rate trends were based on the results of just one trial each. The limit of quantitation (LOQ) was established at 0.01 ppm.

## **COMPLIANCE:**

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. Several minor GLP deviations were noted, although they did not impact the validity of the study.



#### A. BACKGROUND INFORMATION

Pyriproxyfen is an analogue of an insect juvenile hormone and interferes with the hormonal control of insect growth and development, thereby inhibiting egg hatch, larval embryogenesis, metamorphosis, and adult emergence. There are currently three end-use products of pyriproxyfen with food/feed uses that are registered to Valent: two emulsifiable concentrates (EC) and a wettable powder (WP). These formulations are registered for use on bushberry, citrus fruits, cotton, fruiting vegetables, guava, lychee, pome fruits, stone fruits, and tree nuts, and are marketed under the trade names KNACK® Insect Growth Regulator [0.86 lb/gal EC; EPA Reg. No. 59639-95], ESTEEM® Insect Growth Regulator [2.9 lb/gal EC; EPA Reg. No. 59639-104], and ESTEEM® 35 WP Insect Growth Regulator [35% WP; EPA Reg. No. 59639-115].

TABLE A.1.	Cest Compound Nomenclature
Compound	Chemical Structure
C <sub>20</sub> H <sub>19</sub> NO <sub>3</sub>	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
Common name	Pyriproxyfen
IUPAC name	4-phenoxyphenyl (RS)-2-(2-pyridyloxy)propyl ether
CAS name	2-[1-methyl-2-(4-phenoxyphenoxy)ethoxy]pyridine
CAS#	95737-68-1
End-use product/EP	Knack IGR, Esteem IGR



# B. EXPERIMENTAL DESIGN

# **B.1.** Study Site Information

No extreme weather events were noted at any of the field trial sites involved in the present study. Where necessary, irrigation was provided.

TABLE B.	1.1. Study	y Use Pattern.						
Location	EP <sup>1</sup>			Aļ	plication			Tank Mix Adjuvants
(City, State/Year)			Rate, lb a.i./A	RTI (days)	Treat. No.	Method <sup>2</sup>	Total Rate, lb a.i./A	Adjuvants
Martin County, FL/1999	Knack IGR (0.86 EC)	1) 21 (±1) days before harvest 2) 7 (±1) days before harvest	1) 0.066 2) 0.065	14	2	tractor-mounted boom sprayers	0.131	None
Pepin County, WI/1999	Knack IGR (0.86	1) 21 (±1) days before harvest	1) 0.067 2) 0.068	14	2	tractor-mounted boom sprayers	0.135 (1x)	None
	EC)	2) 7 (±1) days before harvest	1) 0.134 2) 0.133				0.267 (2x)	
Uvalde County, TX/1999	Knack IGR (0.86 EC)	1) 21 (±1) days before harvest 2) 7 (±1) days before harvest	1) 0.067 2) 0.069	14	2	tractor-mounted boom sprayers	0.136	None
San Luis Obispo County, CA/1999	Knack IGR (0.86 EC)	1) 21 (±1) days before harvest 2) 7 (±1) days before harvest	1) 0.070 2) 0.066	14	2	tractor-mounted boom sprayers	0.136	None
Martin County, NC/2000	Knack IGR (0.86 EC)	1) 21 (±1) days before harvest 2) 7 (±1) days before harvest	1) 0.066 2) 0.067	14	2	tractor-mounted boom sprayers	0.133	None
San Luis Obispo County, CA/2000	Knack IGR (0.86 EC)	1) 21 (±1) days before harvest 2) 7 (±1) days before harvest	1) 0.067 2) 0.067		2	tractor-mounted boom sprayers	0.134	None



Lehigh County, PA/2000	Knack IGR (0.86 EC)	1) 21 (±1) days before harvest 2) 7 (±1) days	1) 0.067 2) 0.068	14	2	tractor-mounted boom sprayers	0.135	None
		before harvest			:			

<sup>&</sup>lt;sup>1</sup> EP = End-use Product

TABLE B		l Numb													
C	rop		US Growing Regions								Total trials				
· ·=-		1	2	3	4	5	6	7	8	9	10	11	12	13	
Cabbage	Submitted	1	1	1		1	1				2				7
	Requested	1	1	1		1	1				1				6

<sup>&</sup>lt;sup>2</sup> Trials utilized 9.9-10.7 gallons diluted spray per acre.



## **B.2.** Analytical Methodology

The samples were analyzed using minor modifications (equivalent glassware and slightly different GC parameters) to the reference method: "Determination of Pyriproxyfen Residues in Apples, Pears, and Citrus Fruits", Valent method RM-33P-1-3a. In brief, residues of pyriproxyfen were extracted from samples with acetone, partitioned with dichloromethane/water, and cleaned using silica gel column chromatography. Quantitation for pyriproxyfen was by gas chromatography with a nitrogen-phosphorus detector (GC/NPD). The limit of quantitation (LOD) was established at 0.01 ppm; the limit of detection (LOD) estimate was not estimated.

## C. RESULTS AND DISCUSSION

The number of trials and the geographic representation are both adequate for cabbage as a representative commodity of crop group 5, where six field trials are requested (OPPTS 860.1500, Table 2). Significant levels of pyriproxyfen residues were found in the treated cabbage samples containing wrapper leaves. When the wrapper leaves were removed, the pyriproxyfen residue levels were mostly at or below the method LOQ of 0.01 ppm. The residue decline data submitted indicates that pyriproxyfen residues show a slight decrease when the PHI is extended from 3 to 14 days. Doubling the application rate appeared to have little effect on the pyriproxyfen residue level, although this was based on the results of just one trial.

Concurrent recovery results indicate that the data collection method is adequate for detecting pyriproxyfen residues in/on cabbage samples (see Table C.1). Satisfactory recovery values were obtained from cabbage samples spiked at 0.02 and 0.10 ppm. All untreated control samples were free of pyriproxyfen residues and interferences.

The longest harvest-to-analysis interval of any field treated sample was 14 days (Table C.2). The stability of pyriproxyfen residues in frozen cabbage samples was demonstrated by fortification of control samples at 0.10 ppm. The results of this study show that pyriproxyfen residues remain stable in cabbage when stored frozen for 35 days.

As shown in Tables C.3 and C.4, pyriproxyfen residue levels in cabbage samples with wrapper leaves ranged from 0.04-0.49 ppm, while samples without wrapper leaves had pyriproxyfen residues from <0.01-0.02 ppm, when the PHI and RTI were 6-7 and 14 days, respectively. Table C.4 also shows the effect of PHI on pyriproxyfen residue levels in/on cabbage samples with wrapper leaves when the PHI is incremented over a range of 3-14 days. The residue levels show a slight decline over time.



TABLE C.1. Summary of Concurrent Recoveries of Pyriproxyfen from Cabbage.										
Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean ± std dev					
Cabbage	Pyriproxyfen	0.020	9	77-105	91 ± 10					
		0.10	9	77-104	94 ± 8					

TABLE C.2. Summary of Storage Conditions										
Matrix (RAC or Extract)	Storage Temp. (°C)	Longest harvest-to-analysis interval of field samples (days)	Limit of Demonstrated Storage Stability (days)							
Cabbage	<0	14	35							

TABLE C.	.3. R	esidue Data	from Crop Fi	eld Trials w	ith Pyr	iproxyfen.		
Location (City, State/Year)	Region	Crop/ Variety	Application Rate, lbs ai/A	Total Rate, lbs ai/A	RTI (days)	PHI (days)	Residues with Wrapper Leaves (ppm)	Residues without Wrapper Leaves (ppm)
Martin County, FL/1999	3	Cabbage/ Bravo	0.0681 0.0677	0.131	14	7	0.22, 0.21	<0.01, <0.01
Pepin County,	5	Cabbage/ 0.0655 0.135 Supergreen 0.0644		14	7	0.06, 0.11	<0.01, <0.01	
WI/1999			0.136 0.135	0.267 (2x)	14	7	0.06, 0.08	<0.01, <0.01
Uvalde County, TX/1999	6	Cabbage/ Blue Vantage	0.0655 0.0646	0.136	14	6	0.08, 0.08	<0.01, <0.01
San Luis	10	Cabbage/	0.0666	0.136	14	3	0.17, 0.16	ND <sup>a</sup>
Obispo County,		Green	0.0672			7	0.12, 0.08	<0.01, <0.01
CA/1999						10	0.08, <0.01	ND <sup>a</sup>
			6			14	0.15, 0.04	ND <sup>a</sup>
Martin County, NC/2000	2	Cabbage/ Bravo	0.0672 0.0679	0.133	14	7	0.05, 0.04	0.01, 0.01
San Luis Obispo County, CA/2000	10	Cabbage/ Red Rookie	0.0664 0.0661	0.134	14	7	0.16, 0.49	0.02, 0.02
Lehigh County, PA/2000	1	Cabbage/ Market Prize	0.0681 0.0650	0.135	14	7	0.11, 0.11	<0.01, <0.01

Not determined.



TABLE C.4. Summary of Residue Data from Crop Field Trials with Pyriproxyfen.											
Commodity	Total Applic.	PHI (days)	Analyte	Residue Levels (ppm)							
	Rate, lb a.i./A			Min.	Max.	HAFT*	Mean	Std. Dev.			
Cabbage with wrapper leaves	0.132	6-7	Pyriproxyfen	0.04	0.49	0.33	0.14	0.12			
Cabbage without wrapper leaves	0.132	6-7	Pyriproxyfen	<0.01	0.02	0.02	0.011	0.004			

<sup>\*</sup> HAFT = Highest Average Field Trial.

# D. CONCLUSION

The crop field trials for cabbage are classified as acceptable and satisfy the guideline requirements for crop field trials (Residue Chemistry Guidelines OPPTS 860.1500) as they apply to "Vegetable, brassica, leafy, group 5."

## E. STUDY DEFICIENCIES/CLARIFICATIONS

None.